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Paz-Garcia, Juan Manuel; Johannesson, Björn; Ottosen, Lisbeth M.; Alshawabkeh, A. N.; Ribeiro, A. B.; Rodríguez-Maroto, J. M.

Publication date:
2011

Document Version
Publisher's PDF, also known as Version of record

COUPLING THE TRANSPORT OF WATER AND AQUEOUS SPECIES IN FINITE ELEMENT MODELING OF ELECTROKINETICS

J.M. Paz-García[1], B. Johannesson[1], L.M. Ottosen[1], A.N. Alshawabkeh[2], A.B. Ribeiro[3] and J.M. Rodríguez-Maroto[4]

[1] Department of Civil Engineering, Technical University of Denmark;
[2]Department of Civil and Environmental Engineering, Northeastern University, Boston, USA;
[3]Department of Environmental Sciences and Engineering, New University of Lisbon, Portugal;
[4]Department of Chemical Engineering, University of Málaga, Spain

Introduction

The electrokinetic transport of ionic and non-ionic species through a porous media under the effect of an external electric field can be mathematically described by the Nernst-Planck-Poisson (NPP) system of equations.

Mass balance equation for the transport of water:

$$Ap\left(\frac{\partial\theta}{\partial t}\right)=-\nabla\mathbf{J}_\theta+G_\theta;\quad \mathbf{J}_w=\underbrace{-D_\theta\nabla\theta}_{\text{Moisture transport}}\underbrace{-k_h\nabla h}_{\text{Hydraulic transport}}\underbrace{-\theta k_e\nabla\phi}_{\text{Electroosmosis}}$$

Nernst-Planck equation:

$$Ap\theta\left(\frac{\partial n_i}{\partial t}\right)=-\nabla\mathbf{J}_i+G_i;\quad \mathbf{J}_i=\underbrace{\mathbf{v}_w n_i}_{\text{Advection}}\underbrace{-D_i^{eff}\nabla n_i}_{\text{Diffusion}}\underbrace{-U_i^{eff}n_i\nabla\phi}_{\text{Electromigration}}$$

Poisson's equation:

$$\varepsilon\nabla^2\phi=F\sum_{i=1}^{M}n_iz_i$$

where:

• **Advection**	
$\mathbf{v}_w n_i$	Movement of the species in the solution due to the fluid's bulk motion.
• **Diffusion** (Fick's law)	
$-D_i^{eff}\nabla n_i$	Movement of species due to a gradient of chemical potential.
• **Electromigration**	
$-U_i^{eff}n_i\nabla\phi$	Movement of charged species in an electric field.
• **Total Moisture transport** (Richards' equation)	
$-D_\theta\nabla\theta$	Motion of water in unsaturated porous media.
• **Hydraulic flow** (Darcy's law)	
$-k_h\nabla h$	Movement of water in saturated porous media, due to gradient of hydraulic gradients.
• **Electroosmotic flow**	
$-\theta k_e\nabla\phi$	Motion of the liquid induced by an applied electric potential.

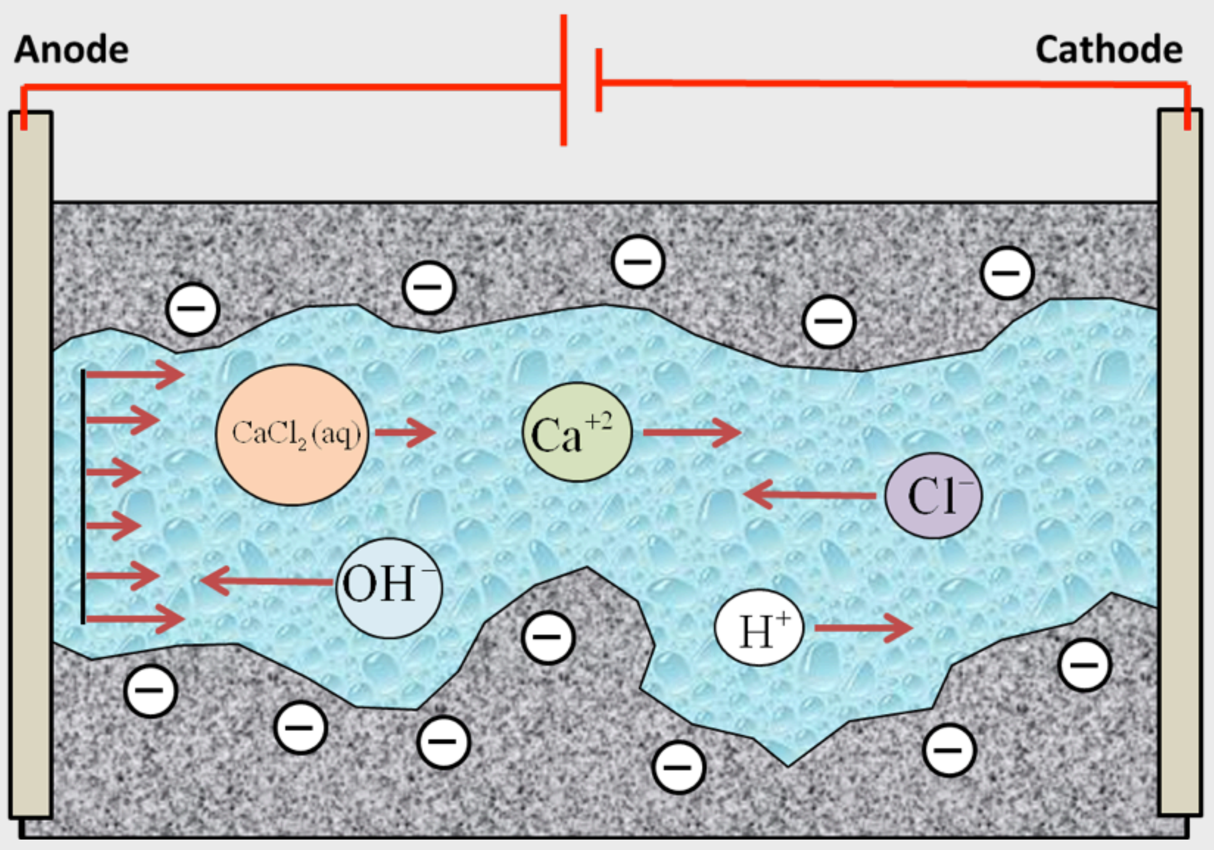

Figure 1: Electrokinetic transport phenomena

1. Electromigration is the main mechanism affecting ionic transport. Electroosmotic advection is important for the transport of non-charged particles.
2. Richards' equation describes the movement of both vapor and liquid water on the basis of a single variable, the moisture content. Capillary forces are assumed the main transport mechanism.
3. The moisture diffusivity is assumed to be non-linear function of the water content and the nature of the porous material.
4. Fully saturated conditions are rare. Hydraulic flow may be negligible with respect to the other transport contributors. Unsaturated conditions are assumed in the proposed numerical model.

Terminology

Table 1: Terminology for the mathematical description of the model

Term:	
$\theta\left(kg_w m_{pore}^{-3}\right)$	Moisture content
$n_i\left(mol_i\,kg_w^{-1}\right)$	Molal concentration
$\phi(V)$	Electrical potential
z_i	Ionic charge
h	Hydraulic head
A	Cross-sectional area
p	Porosity
i	Index for the i^{th} species
M	Total number of aqueous chemical species
$\mathbf{J}$	Flux term
G	Generation term
$\mathbf{v}_w$	Water velocity
D_i^{eff}	Effective diffusivity
U_i^{eff}	Effective ion mobility
D_θ	Total moisture diffusivity
k_e	Electroosmotic permeability coefficient
k_h	Hydraulic conductivity
F	Faraday constant

Table 2: Terminology for the matrices in the Finite Element Formulation.

FEM Matrix	State variable	k parameter
$\mathbf{K}^{mt}$	θ	ApD_θ
$\mathbf{K}^{eo}$	ϕ	$A\theta pk_e$
$\mathbf{K}_i^{mta}$	θ	$ApD_\theta n_i$
$\mathbf{K}_i^{eoa}$	ϕ	$A\theta pk_e n_i$
$\mathbf{K}_i^{dif}$	n_i	$A\theta pD_i^{eff}$
$\mathbf{K}_i^{em}$	ϕ	$A\theta pU_i^{eff}$
$\mathbf{K}_\phi$	ϕ	ε
$\mathbf{E}_i$	n_i	Fz_i
$\mathbf{C}_\theta$	$\frac{\partial\theta}{\partial t}$	$\frac{Ap}{\Delta t}$
$\mathbf{C}_i$	$\frac{\partial n_i}{\partial t}$	$\frac{Ap\theta}{\Delta t}$

Chemical Generation

Water participates in several chemical reactions along the domain of the treated body as, for example, precipitation, dissolution and hydration of salts. In electrokinetics, electrolysis reactions may occur at the electrodes as a consequence of the applied current. And so, water is consume at the vicinities of the electrodes.

$$H_2O \rightleftarrows \frac{1}{2}O_2+2H^++2e^-$$

$$2H_2O+2e^- \rightleftarrows H_2+2OH^-$$

Somewhere in the middle of the treated body, these H^+ and OH^- fronts can meet each other producing water.

Numerical Model

The strongly coupled non-linear NPP system can be satisfactory solved by finite elements integration. It can also be combined to additional physicochemical aspects such as the electrode processes and the chemical interaction between the species in the system for modeling of electrokinetic transport processes.

Let the vector $\mathbf{a}$ be the discrete form at the state variables at the nodal points, and $\mathbf{f}$ the load vectors for the state variables indicated with the corresponding subscript. Generation terms are implicitly included in the load vectors. The weak formula for the extended NPP system in the finite element method is:

Mass balance equation for the transport of water:

$$\mathbf{C}_\theta\left(\mathbf{a}_\theta^t-\mathbf{a}_\theta^{t-\Delta t}\right)+\mathbf{K}^{mt}\mathbf{a}_\theta^t+\mathbf{K}^{eo}\mathbf{a}_\phi^t+\mathbf{f}_\theta=0$$

Nernst-Planck equation:

$$\mathbf{C}_i\left(\mathbf{a}_i^t-\mathbf{a}_i^{t-\Delta t}\right)+\mathbf{K}_i^{mta}\mathbf{a}_\theta^t+\mathbf{K}_i^{dif}\mathbf{a}_i^t+\left(\mathbf{K}_i^{eoa}+\mathbf{K}_i^{em}\right)\mathbf{a}_\phi^t+\mathbf{f}_i=0$$

Poisson's equation:

$$\sum_{i=1}^{M}\mathbf{E}_i\mathbf{a}_i^t+\mathbf{K}_\phi\mathbf{a}_\phi^t+\mathbf{f}_\phi=0$$

A global matrix system of equations is obtained by:

$$\mathbf{C}\left(\mathbf{a}^t-\mathbf{a}^{t-\Delta t}\right)+\mathbf{K}\mathbf{a}^t+\mathbf{f}=0$$

Where:

$$\mathbf{C}=\begin{bmatrix}\mathbf{C}_\theta & 0 & \cdots & \cdots & 0\\ 0 & \mathbf{C}_1 & \ddots & \ddots & 0\\ \vdots & \ddots & \ddots & \ddots & \vdots\\ \vdots & \ddots & \ddots & \mathbf{C}_M & 0\\ 0 & 0 & \cdots & 0 & 0\end{bmatrix};\quad \mathbf{a}^t=\begin{bmatrix}\mathbf{a}_\theta^t\\ \mathbf{a}_1^t\\ \vdots\\ \mathbf{a}_M^t\\ \mathbf{a}_\phi^t\end{bmatrix};\quad \mathbf{f}=\begin{bmatrix}\mathbf{f}_\theta\\ \mathbf{f}_1\\ \vdots\\ \mathbf{f}_M\\ \mathbf{f}_\phi\end{bmatrix};$$

$$\mathbf{K}=\begin{bmatrix}\mathbf{K}^{mt} & 0 & \cdots & \cdots & \mathbf{K}^{eo}\\ \mathbf{K}_1^{mta} & \mathbf{K}_1^{dif} & 0 & \ddots & \left(\mathbf{K}_1^{eoa}+\mathbf{K}_1^{em}\right)\\ \vdots & 0 & \ddots & \ddots & \vdots\\ \mathbf{K}_M^{mta} & \ddots & \ddots & \mathbf{K}_M^{dif} & \left(\mathbf{K}_M^{eoa}+\mathbf{K}_M^{em}\right)\\ 0 & \mathbf{E}_1 & \cdots & \mathbf{E}_M & \mathbf{K}_\phi\end{bmatrix}$$

The proposed system can be used for simulating reactive transport of water and aqueous species in porous material under the effect of an externally applied electric field, as well as for free diffusion problems.

Conclusions

Petrov-Galerkin (PG) or Galerkin least square (PLS) are assumed standard for convection dominated problems, but they required a complicated formulation which usually implies high computation time. By means of the proposed coupled system, including the advective term directly in the Nernst-Planck equation of each aqueous species apart from in the water transport equation itself, the convenience Galerkin method of weighted residuals can be used for the solution of the non-linear coupled transport of water and aqueous species in porous media.

Acknowledgments

Rodriguez-Maroto acknowledges the financial support of the Ministerio de Ciencia e Innovación of the Spanish Government through the project ERHMES, CTM2010-16824. Paz-García acknowledges the Danish Agency of Science Technology and Innovation for the economic support through the project 274-08-0386 "*Fundamentals of Electrokinetics in in-homogeneous matrices*".